The Maxwell-Stefan description of mass transfer in ion exchange and electrodialysis

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Summary

The Maxwell-Stefan equation for mass transfer, which is a more general form of both the Nernst-Planck equation and Fick's law, has been used to describe the unit operations electrodialysis and ion exchange. The parameters required to describe these unit operations have been obtained from empirical relations, equilibrium measurements, dialysis experiments, limiting current experiments, electrodialysis experiments and ion exchange experiments.
Besides the results for the unit operations, which will be discussed separately below, literature data concerning Maxwell-Stefan diffusion coefficients in aqueous electrolyte solutions have been collected. These data formed the starting point for the discovery of the existence of negative Maxwell-Stefan diffusion coefficients in electrolyte solutions and their consistence with the thermodynamics of irreversible processes.

Ion Exchange

The work on the ion exchange process consisted of two parts. Firstly, at low external salt concentrations (≤ 0.1 mol/l), the ion exchange kinetics of systems involving ions with large differences in their ionic mobilities were investigated. At these low salt concentrations the mass transfer rate of the ion exchange process is controlled by the mass transfer resistance in the diffusion film on the outside of the ion exchange particle. It was shown both experimentally and theoretically, that the ion exchange kinetics for the NaCl/HCl and $CaCl_2$/HCl systems were asymmetric, due to the potential difference which was generated by the difference in the ionic mobilities of the two cations. In the case where the hydrogen ion (with the larger ionic mobility) was diffusing from the solution into the ion exchange resin, the electrical potential enhanced the mass transfer and vice versa.
Secondly, at high external salt concentrations (1 mol/l), the breakthrough curves of a packed ion exchange column using the NaCl/HCl system were investigated. At these higher concentrations, the ion exchange process is controlled by the mass transfer resistance inside the ion exchange particle. The aim of this project was to determine whether or not the breakthrough curves could provide useful information concerning the Maxwell-Stefan diffusion coefficients in ion exchange resins. It was found that although not all the diffusion coefficients could be obtained, useful information concerning the cation-resin and cation-cation diffusion coefficients could be obtained from the breakthrough curves. It should however be noted that accurate information concerning column hydrodynamics, particle size and especially equilibrium data is a prerequisite for the determination of accurate diffusion coefficients.
In general it can be concluded from the work presented in this thesis, that the Maxwell-Stefan equation provides a suitable description for the ion exchange process.

Electrodialysis

The number of parameters required for the complete description of the electrodialysis process is large, and hence a number of independent experiment were used, so that reasonable estimates of all the parameters could be obtained. In the first part of the work presented in this thesis, the model system consisting of aqueous NaCl/HCl solutions was investigated.

Firstly, the Ionics membranes (204 UZL 386 and 61 CZL 386) were characterised completely. The ion exchange capacity, membrane thickness, water content, electrolyte sorption of both membranes were determined as a function of the external NaCl or HCl concentration.

Secondly, limiting current measurements were performed to obtain information about the thickness of the polarisation films on both sides of the membranes. In order to obtain a more exact method for the determination of the limiting current, a model consisting of a number of resistances in series, and using the phenomena of charge separation, was developed. Using this model a Cowan plot could be described mathematically, and a less arbitrary value for the polarisation film thickness could be obtained from this plot.

Thirdly, a number of dialysis experiments were performed. In each of these experiments, only one salt and one membrane were used. From these experiments the Maxwell-Stefan diffusion coefficients involving the co-ions could be obtained. The remainder of the Maxwell-Stefan diffusion coefficients were obtained from empirical relations.

And finally, actual electrodialysis experiments were performed, and from these experiments the remaining unknown parameters were determined. From the experiments with the NaCl/HCl system, it was found, that the electrodialysis process could not be modelled as a pure diffusive process. Or in other words, in an electrodialysis stack, other phenomena occur besides normal diffusion. These phenomena include the current leakage through fluid transport channels, viscous convection and ordinary leakage. Only if these mechanisms are all taken into account properly, can the Maxwell-Stefan diffusion coefficients inside the ion exchange membrane be determined accurately. For the NaCl/HCl system a set of diffusion coefficients was determined, which could be used for salt concentrations between 0.1 and 1.0 mol/l.

The electrodialysis of the more complex system consisting of two amino acids with different isoelectrical points was also examined. It was found that the fraction of the current used for the transport of each of the amino acids through the membranes depended on the pH of the solution from which they were removed. This effect of the pH on the efficiency of the amino acid transport, could be described using the Maxwell-Stefan equations. Unfortunately, due to experimental inaccuracies it was however not possible to obtain a very reliable set of diffusion coefficients

Again in general, it may be concluded, that the Maxwell-Stefan theory provides an adequate basis for the description of the electrodialysis process, It must however be born in mind that in this unit operation other (non-diffusive) phenomena may occur.